

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
12 July 2001 (12.07.2001)

PCT

(10) International Publication Number
WO 01/49621 A1

(51) International Patent Classification?: C03C 3/064, 3/066, 3/085, 3/091, 3/093, 8/02, 8/04, 8/06, H01J 17/18

(72) Inventor; and

(75) Inventor/Applicant (for US only): YOUNG, Dianna, M. [US/US]; 54 West Fourth Street, Corning, NY 14830 (US).

(21) International Application Number: PCT/US00/30225

(74) Agent: KUNG, Vincent, T.; Corning Incorporated, SP TI 3 1, Corning, NY 14831 (US).

(22) International Filing Date:
2 November 2000 (02.11.2000)

(25) Filing Language:

English

(81) Designated States (national): CA, CN, JP, KR, US.

(26) Publication Language:

English

(84) Designated States (regional): European patent (DE, FR, NL, TR).

(30) Priority Data:

60/174,011 30 December 1999 (30.12.1999) US
09/585,135 1 June 2000 (01.06.2000) US

Published:

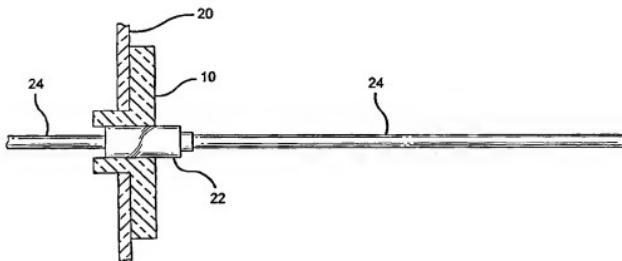
— With international search report.

(71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



(54) Title: COPPER ALUMINO-SILICATE GLASSES

(57) Abstract: The present invention is directed to a copper aluminosilicate glass having coefficients of thermal expansion (CTEs) of $20.82 \times 10^{-7}/^{\circ}\text{C}$ (over a range of $25\text{--}500\ ^{\circ}\text{C}$) and softening points of $660\text{--}1000\ ^{\circ}\text{C}$. The glass is useful as a preformed sealing glass. For example, in a vacuum lamp, a solder glass preform ring (10) of the inventive copper aluminosilicate glass fits against a glass wall (11) and a glass bead sleeve (22). An electrode lead wire (24) passes through the glass sleeve (22). The preferred copper aluminosilicate glass has a composition, in weight percent, of: SiO_2 35-68, Al_2O_3 3-25, B_2O_3 2-26, R_2O 0-20, RO 1-30, CuO 2-33, F 0-4, M_1O 0-10, R_2O is an alkali metal oxide selected from Li_2O , Na_2O , and K_2O . RO is an alkaline earth metal oxide selected from CaO , MgO , ZnO , SrO , and BaO . M_1O is a transition metal oxide selected from Co_2O_3 , TiO_2 , NiO , MnO_2 , and Fe_2O_3 .**WO 01/49621 A1**

TITLE OF INVENTION**COPPER ALUMINO-SILICATE GLASSES**5 **CROSS-REFERENCE TO RELATED APPLICATIONS**

An application entitled FUSION SEALED ARTICLE AND METHOD, which was filed on July 30, 1999, having U. S. Serial Number 09/364,141, from U.S. Provisional, Serial Number 60/107,379, filed on November 6, 1998, in the name of Dianna M. Young, and assigned to the same assignee as this application, is directed to a fusion seal for a telecommunication device, the fusion seal being a copper aluminosilicate glass that has a softening point less than 900°C and CTE less than about $20 \times 10^{-7}/^{\circ}\text{C}$.

PRIORITY CLAIM

15 This application claims priority from an application entitled COPPER ALUMINOSILICATE GLASSES, which was filed as U.S. Provisional, Serial Number 60/174,011, on December 30, 1999, in the name of Dianna M. Young, and assigned to the same assignee as this application.

20 **BACKGROUND OF THE INVENTION**1. **FIELD OF INVENTION**

The present invention relates to copper aluminosilicate glasses, and in particular to such copper aluminosilicate suitable for sealing borosilicate glasses or glass-ceramic materials.

2. DESCRIPTION OF THE RELATED ART

The joining of component parts together by means of a fused glass seal to form a composite article is a well-cultivated art. In particular, numerous special sealing glasses have been developed for use in joining glass parts with each other, or with metals, alloys, or ceramics. In making a fusion-type seal, the sealing material must be heated to a temperature where it becomes soft enough to wet the sealing surface and form an adhesive, hermetic bond.

The type of glass used in forming a fusion-type seal varies according to the desired properties of the article being sealed. For many purposes, manufacturers want to keep the softening temperature (softening point) as low as possible, while also maintaining a low to medium coefficient of thermal expansion (CTE). This is particularly true for lamp work having electrical and electronic articles where thermally sensitive parts or coatings are commonly used.

Typically, electrical lamps employ borosilicate glass envelopes or bulbs and require joining or sealing of these envelopes to either another piece of glass or metal (usually electrodes) to achieve hermeticity within the glass vessel. Borosilicate glass has a coefficient of thermal expansion (CTE) of $30 - 40 \times 10^{-7}/^{\circ}\text{C}$. The normal CTE for borosilicate lamp glasses, such as Pyrex[®] by

Corning, is $38 \times 10^{-7}/^{\circ}\text{C}$. The elements enclosed in the glass vessel may include phosphor coatings (fluorescent lamps), metal electrodes, or metallic reflective coatings. Coatings and electrodes require a hermetic environment, otherwise their properties diminish, and as a result the lifetime of the device is dramatically shortened. The coatings elements, however, are typically sensitive to relatively high temperatures, especially greater than 600°C , and thus sealing temperatures must be maintained low, and processing times must be maintained short to avoid decomposition or degradation of these components.

The current workable sealing glasses used in lamps of the type described above are phosphate based frits. Phosphate frits have the advantage of low softening points and, hence, are considered low temperature sealing glasses. Solder glasses currently available can be classified in two

categories: 1) leaded phosphate sealing glasses and 2) non-leaded phosphate sealing glasses. Both categories contain compositions that can be classified as vitreous or crystallized, in which crystallized sealing glasses are resistant to deformation under the conditions of reheating in vacuum – an advantage, for example, in television manufacture applications. In the prior art, medium expansion of sealing glasses is established typically by adding low expansion fillers (usually cordierite, lithium alumino-silicate glass-ceramics, or crystalline cobalt pyrophosphate, or magnesium pyrophosphate) to relatively high expansion base glass compositions ($60\text{--}120 \times 10^{-7}/^{\circ}\text{C}$) that have a relatively low softening points (350 - 400°C).

The two categories of phosphate sealing glasses mentioned above, however, suffer from a number of disadvantages. First, as stated before, to bring down the CTE, phosphate glasses require adding substantial amounts of fillers. The fillers can add significantly to the overall cost of the glass frit.

Second, the addition of filler mandates that the sealing glass be used in a powdered form, which is less desirable for tubular geometries. Third, these phosphate frits tend to create seals that are not consistently hermetic when used to seal borosilicate glass, particularly when a desired application calls for the use of a tube geometry. Phosphate glass frits by their inherent nature need to be used in either a dry powder or paste form. Air permeates the seal because the frit powder or paste does not densify completely. Gaps and pores often will appear during the sintering process as the organic binders in the paste de-gas when burned-out under high temperatures. Additionally, as the phosphate frit melts, the glass tends to flow under gravity towards the bottom.

Even though, phosphate frits can seal flat glass applications without much problems, some gaps or pores, however small, will always exist between the frit particles in complex geometric applications aside from flat glasses. Moreover, it is difficult to cover or seal certain geometric configurations, such as round or cylindrical forms with loose powder or even paste. Since sealing glasses used in the powdered form is susceptible to porosity within the seal, hermeticity is harder to achieve in the seal.

At the present time, a need for improvement continues to be unsatisfied in the medium-expansion sealing/solder glass industry, especially in seals for electrical lamp constructions such as photoflash lamps, vehicle headlamps and lamps for fluorescent lighting. If one has to use a solder glass to join together 5 various glass articles or pieces that are characterized as having medium expansion, one has limited options.

It is known that all of the various monovalent and divalent oxides are effective in reducing the melting temperature of glass frit. The fluxing power of 10 these oxides is as follows, in decreasing order: $\text{Li}_2\text{O} > \text{PbO} > \text{Na}_2\text{O} > \text{K}_2\text{O} >$ $\text{BaO} > \text{CaO} > \text{SrO} > \text{MgO} > \text{ZnO}$. Replacement of silica by B_2O_3 decreases the melting temperature, as does a decrease in the silica, zirconia, and alumina content. Moreover, use of several fluxing ingredients in proper proportion is more effective in decreasing the melting temperature than use of any single 15 oxide. It is also known that in general, those oxides that have the greatest fluxing power give the highest expansion.

Sealing glasses composed essentially of copper aluminum and silicon oxides are also known in the art. In contrast to phosphate glasses, these copper glasses have low to medium coefficients of thermal expansion that typically do not exceed $20 \times 10^{-7} /^\circ\text{C}$, but rather are lower than $10 \times 10^{-7} /^\circ\text{C}$, 20 over a broad temperature range. Briefly studied in the 1960s and early 1970s, this property made copper alumino-silicates a favored type of sealing glass for joining fused silica, fused quartz, and other low-expansion glass and glass-ceramics materials.

To illustrate, the following patents describe some of the qualities and 25 applications of copper sealing glasses that are known. U.S. Pat. No. 3,414,465 (Baak *et al.*) discloses a copper sealing glass used for forming fused quartz to fused quartz seals and fused silica-to fused silica seals. The glass has a composition of 50-90 mol % SiO_2 , 5-30 mol % Al_2O_3 , 5-30 mol % Cu_2O , 0-6 mol % NiO , 0-6 mol % Fe_2O_3 , and 0-6 mol % AlF_3 . The '465 patent describes the 30 copper sealing glasses composition as generally having a coefficient of linear thermal expansion of not more than about $10 \times 10^{-7} /^\circ\text{C}$ in the temperature range of 0 - 300°C.

U.S. Pat. No. 3,445,212 (Bishop) teaches a method of sealing a copper lead-in conductor to a surface of a low-expansion silica containing material using a reduced copper sealing glass. The sealing glass is selected from the group of glasses consisting of 75-80 mol % SiO₂, 8-12 mol % Al₂O₃, 10-15 mol % Cu₂O, and a glass consisting of 75-80 mol % SiO₂, 8-12 mol % Al₂O₃, 10-15 mol % Cu₂O, and 1-3 mol % AlF₃. The glass composition described in the '212 patent is designed to seal low expansion ceramic, fused quartz or silica bodies with a coefficient of expansion of about $20 \times 10^{-7}/^{\circ}\text{C}$ or preferably less in the temperature range of 0 - 300°C.

U.S. Pat. No. 3,451,579 (Bishop) discloses a vitreous solder glass composition for bonding a fused silica window to a ceramic body lamp, the composition consisting of 75-80 mol % SiO₂, 8-12 mol % Al₂O₃, 10-15 mol % Cu₂O. The '579 patent further discloses a sealing glass consisting of 75-80 mol % SiO₂, 8-12 mol % Al₂O₃, 10-15 mol % Cu₂O, and 1-3 mol % AlF₃, with a coefficient of expansion of $4-10 \times 10^{-7}/^{\circ}\text{C}$ over the temperature range of 0 - 300°C.

U.S. Pat. No. 3,459,569 (Ellis) discloses glass compositions for sealing and decorating low expansion glass-ceramic materials and borosilicate type glasses. The glass compositions contain 55-70 mol % SiO₂, 6-10 mol % Al₂O₃, 0-2.5 mol % MnO₂, 0-3 mol % Fe₂O₃, 5-12 mol % Cu₂O, and 10-22 mol % Li₂O.

U.S. Pat. No. 3,498,876 (Baak et al.) describes copper-zinc alumino-silicate glasses for sealing with low thermal expansion materials such as fused quartz and fused silica. The glasses have compositions consisting essentially of 50-94 mol % SiO₂, 0.5-30 mol % Al₂O₃, 1.5-35 total mol % Cu₂O and CuO, and 0.5-20 mol % ZnO; and generally exhibit coefficients of thermal expansion that are not greater than $15 \times 10^{-7}/^{\circ}\text{C}$ over the temperature range of 0 - 300°C.

U.S. Pat. No. 3,528,829 (Baak et al.) reveals glasses that contain copper and are useful for sealing fused quartz, as well as ceramics, metals and related materials. These glasses have compositions consisting essentially of 72-85 mol % SiO₂, 2-15 mol % Al₂O₃, 2-15 mol % Cu₂O, and 1-10 mol % ZnO. The glass composition has a coefficient of thermal expansion of about $10 - 11 \times 10^{-7}/^{\circ}\text{C}$ in the temperature range of 0 - 300°C.

U.S. Pat. No. 3,779,781 (Baak et al.) describes copper alumino-silicate glass compositions containing as essential components 50-94 mol % SiO₂, 0.5-30 mol % Al₂O₃, 1.5-35 mol % Cu₂O, where there is at least 60 mol % silica in ternary compositions. The glasses disclosed are useful as sealing glasses,
5 particularly for fused quartz, since they have a relatively low melting point and coefficients of thermal expansion less than 10 x10⁻⁷ /°C or less over the temperature range of 0 - 300°C.

Commercially available copper alumino-silicate sealing glasses have been tested and found to be wanting for sealing borosilicates or other glass
10 systems of medium expansion. Although they form a rigid vitreous seal, these glasses exhibit a tendency to have softening points in excess of 900°C. This means that these glasses require high sealing temperatures, which are not only difficult to control, but also will damage, if not decompose, temperature
15 sensitive electrical components in the articles or devices, such as lamps, to be sealed. Further, these glasses require melting temperatures over 1500°C., and have coefficients of thermal expansion that tend to be lower than desired.

Consequently, a need to formulate a type of sealing glass, without the shortcomings of phosphate glasses, but with relatively low softening points and low-medium to high coefficients of thermal expansion, especially suited for
20 borosilicate glasses, continues until the present time. This need has prompted us to further experiment and produce the present, inventive glass compositions.

BRIEF SUMMARY OF THE INVENTION

The present invention comprises a copper alumino-silicate glass
25 composition that can better serve as a sealing material for borosilicate articles or other glass systems of medium expansion because of the composition's comparable thermal expansion at low temperatures. Another advantageous feature of the inventive glass composition is the relatively low softening point. The inventive glasses can be sealed at such temperatures and within such times as that it will not cause decomposition or degradation to temperature
30 sensitive components, such as coatings and electrodes in electrical lamps or other lighting devices. Additionally, unlike phosphate frits, the present invention

provides a sealing glass that may be used both in frit powder form or solid, nonporous, glass bodies of various geometries, such as disks, washers, canes, or tubes. These and other aspects, features and advantages of these inventions will become evident from the following detailed description of the

5 invention.

One aspect of the inventive copper alumino-silicate glasses has coefficients of thermal expansion (CTEs) between $20\text{--}82 \times 10^{-7}/^{\circ}\text{C}$ (over a range of $25\text{--}500\ ^{\circ}\text{C}$) and softening points between $660\text{--}1000\ ^{\circ}\text{C}$. These characteristics make the new glass composition suitable for use as a sealing glass, especially for borosilicate glasses since the inventive composition have relatively comparable or similar, and inclusive coefficients of thermal expansion with borosilicates. The new glass compositions, in terms of weight percent on an oxide basis, consist essentially of $35\text{--}68\ \text{SiO}_2$, $3\text{--}25\ \text{Al}_2\text{O}_3$, $2\text{--}26\ \text{B}_2\text{O}_3$, $2\text{--}33\ \text{CuO}$, $0\text{--}20\ \text{R}_2\text{O}$, $1\text{--}30\ \text{RO}$, $0\text{--}4\ \text{F}$, $0\text{--}10\ \text{M}_x\text{O}_y$, where R_2O is an alkali oxide selected from the group consisting of Li_2O , Na_2O , K_2O , and RO is an alkaline earth oxide selected from the group consisting of CaO , MgO , ZnO , SrO , BaO , and M_xO_y is a transition metal oxide selected from the group consisting of Co_2O_3 , TiO_2 , NiO , MnO_2 , and Fe_2O_3 . A preferred composition range consists essentially, in terms of weight percent on an oxide basis, of $61\text{--}67\ \text{SiO}_2$, $3\text{--}5\ \text{Al}_2\text{O}_3$, $22\text{--}26\ \text{B}_2\text{O}_3$, $3\text{--}9\ \text{CuO}$, $1\text{--}4\ \text{R}_2\text{O}$, $0\text{--}4\ \text{F}$, where R_2O is an alkali oxide selected from the group consisting of Li_2O , Na_2O , K_2O .

BRIEF DESCRIPTION OF FIGURES

- FIGURE 1. A schematic, cross-sectional view of a hermetic seal made using 25 a solder glass preform ring with a glass beaded electrode wire lead.
- FIGURE 2. A schematic, cross-sectional view of a tubulation seal made using a solder glass preform washer.
- FIGURE 3. A schematic, cross sectional view of a plug seal made using a 30 solder glass preform plug.

DETAILED DESCRIPTION OF THE INVENTION

In contrast to copper alumino-silicate glasses that in the past have CTEs typically lower than $10 \times 10^{-7}/^{\circ}\text{C}$, recent work has produced copper alumino-silicates, with higher coefficients of thermal expansion and softening points less than 900°C . These copper glasses are used to sealing glasses for
5 telecommunication devices, as described in US Patent Application No. 09/364,141, herein incorporated in its entirety by reference. Nonetheless, the CTEs of these glasses still remained less than $20 \times 10^{-7}/^{\circ}\text{C}$. From that study evolved a search for copper alumino-silicate glasses that would be more effective as sealing glasses for a gamut of glasses with low-medium to high
10 thermal expansions. The present invention is a result. The inventive copper alumino-silicate glasses exhibit CTEs in the range of $20-82 \times 10^{-7}/^{\circ}\text{C}$. We believe that the inventive glass compositions are more suited for sealing borosilicate glasses that have CTEs in the range of $30-40 \times 10^{-7}/^{\circ}\text{C}$, as well as, any other glass system having a low-medium to high CTE within the range of
15 $20-82 \times 10^{-7}/^{\circ}\text{C}$, (e.g.: Code #1723 an alumino-silicate, #8082, #8083, #8087 lead silicates, #8088 a borate, all of which are commercially available from Corning Inc.).

We discovered that by substituting alkali oxides or alkaline earth oxides for copper in the composition of the glasses, the coefficient of thermal
20 expansion for copper alumino-silicate glass could be raised to a desired value that can match the CTE of a material to be sealed, such as borosilicates. This characteristic is an important feature of the present invention. The alkali or alkaline earth oxides, along with boric oxide and fluorine, serve principally as glass network modifiers, which lowers the softening point of the glass and promotes fluxing. The alkali metal cations disrupt the highly covalent silicon-oxide network where covalent linkages are partially removed or destroyed. The overall effect is to weaken the network structure. The positively charged
25 interstitial regions counter-balance the negatively charged network regions of the silicon-oxide. With the addition of fluorine, we terminate some of the continuous network structure by breaking the silicon-oxygen bonds. This lowers the softening temperatures of the different embodiments of the inventive glass composition. Additionally, even though boric oxide is present in the
30

composition as a network former, boric oxide can still acts as a softener for alumino-silicate glasses. Because boron is only trigonally bound to the network, as contrasted to the tetra bond of silicate, the network that boric oxide produces is easier to disrupt than a network formed from silicate.

5 The copper aluminosilicate sealing glasses of the present invention, as calculated on an oxide basis in weight percent, consist essentially of: 35-68% SiO₂, 3-25% Al₂O₃, 2-26% B₂O₃, 2-33% CuO, 0-20% R₂O, 1-30% RO, 0-4% F, 0-10% M_xO_y, where R₂O is an alkali oxide selected from the group consisting of Na₂O, Li₂O, K₂O, and RO is an alkaline earth oxide selected from the group 10 consisting of CaO, MgO, ZnO, SrO, BaO, and M_xO_y is a transition metal oxide selected from the group consisting of Co₂O₃ TiO₂, NiO, MnO₂ and Fe₂O₃. The glasses of the present invention exhibit CTEs in the range of 20-82 x 10⁻⁷/°C over the temperature range of 25-500°C, and have softening points on the order of 660-1000°C. Although these softening points are higher than the 15 temperatures at which degradation and decomposition in lamp components take place (i.e., about 600°C), the present inventive glasses are still suitable as sealing glasses.

In all sealing applications the solder glass is used to provide a hermetic seal to replace the more traditional method of glass-to-glass flame sealing, 20 which requires pre-heating of parts to elevate temperatures above the anneal point of the glass (>550°C). In lamps that are phosphor coated, an embodiment of lighting devices that would likely incorporate the inventive glasses in their manufacture, we desire to keep the phosphor coating from damage. Thus, it is more advantageous to limit prolonged exposure of the 25 lamp body to elevated temperatures.

Even though the copper solder glasses can either be heated using traditional convection heating or heated locally, we discovered that the glasses of the present invention sealed faster when we use small area sealing techniques. The glasses melted more quickly when subjected to infrared (IR) 30 irradiation or any other source that emits long wavelength energy of one micron or longer, such as a pin-point sealing CO₂ laser, hydrogen/oxygen flame, or their equivalents. In these techniques, quick melting minimizes heat flow to

the rest of the article being sealed. During the soldering process, we apply heat energy in a direct, concentrated and intense fashion to a small portion of the article, at the solder joint where the inventive sealing glasses will be melted. The inventive sealing glass being irradiated at that portion absorbs the
5 irradiation more efficiently, and heats faster than the rest of the glass of the article, which induces faster melting of the sealing glass and sealing of the article. While the temperature of the small area that had the heating source focused upon it rises and becomes hot enough to melt, the rest of the glass article containing the electrical lamp and its electrical components remains
10 relatively cool. Those sensitive components and their surrounding glass structures in the article are protected and exposed to the least amount of heat necessary during the soldering process. For example, because the substrate glass that forms the envelope of an electrical lamp is a different type of glass, such as borosilicate, than the leaded copper sealing glass, which has a
15 particular affinity to long-wavelength energy heating, the envelope does not absorb long wavelengths such as infrared. Thus, the lamp and electrical components are not heated to the point where degradation and decomposition can even begin to occur.

Not intending to be bound by theory, we believe that the lower melting
20 temperature of the inventive glasses, described above, is a function of the composition and particularly due to the copper being in the glass. The glasses contain both cupric, Cu²⁺, and cuprous copper ions, Cu¹⁺. Both types of copper ions absorb in the infrared wavelengths. Because the copper ions are more easily excited by electromagnetic waves having wavelengths of one micron or
25 longer, the new copper glasses absorb infrared irradiation more efficiently than the substrate glass that forms the lamp envelope. For this reason, copper ions aid in the absorption of long wavelengths used in spot heating the sealing glass during the soldering process. The lamp envelope glass does not readily absorb at one micron, or absorbs very little at that wavelength.

As mentioned before, the currently workable glasses used in sealing
30 lamps made of borosilicates are phosphate based frits. In contrast to the shortcomings of phosphate sealing glasses, the inventive copper alumino-

silicate glasses can be manipulated into various physical forms, a novel feature of the invention. They may be formed into solid geometries, such as bulk glass, disks, washers, drawn as cane, tubes, ribbon, or fiber, as well as pulverized to into conventional glass sealing frit powder. Being able to use the
5 glass in various forms permits maximum flexibility for us to accommodate complex geometries when glass sealing of electrical lamps or optical components. Using the inventive copper glass in the form of bulk glass, disks, washer, cane, tubing, fiber, or ribbon not only eliminates the problems
10 associated with sintering conventional frit powder applications, because the sealing glass can conform to the shape of the required seal, but it can also minimize or even eliminate the pores that are left within the seal as a natural consequence when frit powder is melted. Hence, we more readily achieve hermeticity of the seal.

These properties are optimized in a family of preferred compositions, again in weight percent on a calculated oxide basis, that consist essentially of:
15 61-67% SiO₂, 3-5% Al₂O₃, 22-26% B₂O₃, 3-9% CuO, 1-4% R₂O, 0-4% F, where R₂O is an alkali oxide selected from the group consisting of Li₂O, Na₂O, K₂O. These preferred copper aluminosilicate glasses have CTEs in the range
20 of 36-40 x 10⁻⁷/°C over the temperature range of 25-500°C, and softening points of about 600-750°C.

When we prepared the glass compositions of the present invention, we formulated and mixed batches of glass in conventional manner. The batch ingredients were compounded, and thoroughly mixed together to secure a homogeneous melt. We melted each batch of the starting compounds, in their
25 respective proportions, in silica crucibles at temperatures ranging from 1200-1500°C for 4 hours in an electric furnace. At the end of the four hours, we poured the glass melt onto steel plates to provide the test pieces for physical analysis. These glass pieces were transferred and annealed at temperatures ranging from 400-500°C. The glasses produced by this process exhibited a
30 dark green to blackish color. Table A. summarizes several examples of the glass compositions of the present invention, where the respective amounts of the starting oxides are specified, and the respective coefficient of thermal

expansion and resulting softening points are reported. These examples are merely illustrative and not to be construed as limiting the invention.

TABLE A

5 Copper alumino-silicate Compositions, Thermal Expansion, & Softening Point

		Oxides (wt %)							
	Example No.	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CuO	R ₂ O	F	CTE ($\alpha \times 10^{-7}/^{\circ}\text{C}$)	Soft. Pt. (°C)
10	1.	67.2	3.21	23.9	2.51	3.91 (Na ₂ O)	—	37.2	704
	2.	64.9	3.10	22.3	2.42	3.77 (Na ₂ O)	3.43	39.7	689
	3.	61.7	3.41	24.9	6.05	3.77 (Na ₂ O)	—	40.0	703
	4.	61.6	3.41	24.8	7.25	3.77 (Na ₂ O)	—	37.8	721
	5.	61.4	3.40	24.8	8.43	1.88 (Na ₂ O)	—	34.6	692
	6.	62.7	3.47	25.3	3.69	3.83 (Na ₂ O)	—	41.4	688
15	7.	63.0	3.49	25.4	3.71	2.89 (Na ₂ O)	—	39.3	702
	8.	63.3	3.50	25.5	3.73	1.94 (Na ₂ O)	—	38.8	718
	9.	64.0	3.54	25.8	3.76	2.83 (Li ₂ O)	—	36.0	682
						0.92 (Li ₂ O)			
20						1.39 (Li ₂ O)			
						1.94 (Na ₂ O)	—		
						1.87 (Li ₂ O)	—		
						2.83 (Li ₂ O)	—		

Persons working in the art can recognize that, whereas the process described above is directed toward laboratory activity, the glasses operable in the invention can be melted in large commercial melting units and formed into desired shapes by conventional glass melting and forming practices. The compositions need to be fired at sufficiently high temperatures and for a sufficient period of time to produce a homogeneous melt. Thereafter, the melt can be cooled and simultaneously shaped into a glass preform that is annealed and prepared for use as a seal.

Figures 1 through 3 exemplify in schematic drawings a few of the many different uses for hermetic sealing, which we have experimented, of the inventive glass composition. The illustrations show cross-sectional views of "preform" shapes in various geometries as the glass seals could look like prior to heating and subsequent "flow" to produce the hermetic seal. The material can also be in "paste" form to do the same thing, but as discussed earlier, the inventive glasses permitted solid forms an easier task to draw in geometrical shapes. Figure 1 shows in cross-section a hermetic seal for an electrode. The seal is made by using a solder glass preform ring (10) that fits against a glass wall (20) and a glass (bead) sleeve (22) with an electrode lead wire (24) passing through it. This type of seal is currently being used in lighting articles and devices such as vacuum lamps (incandescent, fluorescent, HID), and may

be usable in the art of telecommunication devices or opto-photonic components in the foreseeable future. Figure 2 illustrates an example of a tubulation seal made using a solder glass preform washer-ring (30). This type of seal joins a glass tube (32) with a glass wall (34) of an article or device. To illustrate a use
5 of this kind of seal, during lamp processing, exhaust tubulations of typical vacuum lamps are used for the purpose of providing a temporary connection to an exhaust machine. During a typical exhaust process, a lamp is evacuated and back-filled with inert gas through the exhaust tube. As a final step, the exhaust tube is heated (tipped-off) by flame and the lamp removed, resulting in
10 a hermetically sealed lamp. Figure 3 shows a simple plug seal made using a solder glass preform plug (40) of an opening in the glass wall (42) of an article or device. Plug seals can be used in flat panel displays (FPD), for example, where lamps are processed without exhaust tubulations in a vacuum chamber. Flat panel displays have become quite prevalent as substrates in liquid crystal
15 display devices and the emerging flat TV technologies. A plug seal provides a means of hermetically sealing the FPD after evacuating and back-filling. In some cases, the inventive glass is particularly adaptive as a solder glass to hermetically seal holes after phosphor filling and draining.

The inventive copper glasses described herein are suitable for sealing a
20 variety of medium expansion glasses, where borosilicates are a primary example. Nonetheless, any medium expansion glass or glass-ceramic materials could be also sealed with these copper glass compositions, using the various physical forms into which the glass can be molded. Although the present invention has been fully described by way of examples, it is to be noted
25 that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the present invention, they should be construed as included therein.

CLAIMS

1. A copper aluminosilicate glass having a composition, as expressed in weight percent on an oxide basis, consisting essentially of:

5	SiO ₂	35-68%
	Al ₂ O ₃	3-25
	B ₂ O ₃	2-26
	R ₂ O	0-20
	RO	1-30
10	CuO	2-33
	F	0-4
	M _x O _y	0-10

where R₂O is an alkali oxide selected from the group consisting of Li₂O, Na₂O, K₂O, RO is an alkaline earth oxide selected from the group consisting of CaO, MgO, ZnO, SrO, BaO, and M_xO_y is a transition metal oxide selected from the group consisting of Co₂O₃, TiO₂, NiO, MnO₂, and Fe₂O₃.

- 20 2. The copper aluminosilicate glass of Claim 1, wherein the composition has a CTE in the range of 20-82 × 10⁻⁷/°C over the temperature range of 25-500°C, and has a softening point of 660-1000°C.
- 25 3. A copper alumino-silicate glass having a composition, as expressed in weight percent, that consists essentially of:

30	SiO ₂	35-68%
	Al ₂ O ₃	3-25
	B ₂ O ₃	2-26
	R ₂ O	0-20
	RO	1-30
	CuO	2-33
	F	0-4
	M _x O _y	0-10

35 where R₂O is an alkali oxide selected from the group consisting of Li₂O, Na₂O, K₂O, RO is an alkaline earth oxide selected from the group consisting of CaO, MgO, ZnO, SrO, BaO, and M_xO_y is a transition metal oxide selected from the group consisting of Co₂O₃, TiO₂, NiO, MnO₂,

and Fe_2O_3 , and has a coefficient of thermal expansion in the range of $20-82 \times 10^{-7}/^\circ\text{C}$ over the temperature range of $25-500^\circ\text{C}$, and has a softening point within the range of $660-1000^\circ\text{C}$.

- 5 4. The copper alumino-silicate glass of Claim 1, wherein said composition, in weight percent on an oxide basis, preferably consists essentially of:

	SiO_2	61-67%
	Al_2O_3	3-5
	B_2O_3	22-26
10	CuO	3-9
	R_2O	1-4
	F	0-4

15 where R_2O is an alkali oxide selected from the group consisting of Li_2O , Na_2O , K_2O , and said glass has a CTE in the range of $36-40 \times 10^{-7}/^\circ\text{C}$ over the temperature range of $25-500^\circ\text{C}$, and a softening point from $660-750^\circ\text{C}$.

- 20 5. The copper alumino-silicate glass of Claim 3, wherein said glass is a sealing glass used with an article having a coefficient of thermal expansion of $20-82 \times 10^{-7}/^\circ\text{C}$ over the temperature range of $25-500^\circ\text{C}$.
- 25 6. The copper alumino-silicate glass of Claim 3, wherein said glass is a sealing glass that has a solid geometric form.
7. The solid geometric form of Claim 6, wherein said form is one of the following: a bulk glass, disk, washer, cane, tube, ribbon, or fiber.
- 30 8. The copper alumino-silicate glass of Claim 3, wherein said glass is a sealing glass that has a form, wherein said form is either frit or paste.
9. The copper alumino-silicate glass of Claim 3, wherein said glass is a sealing glass used with glass articles made from materials consisting of:

borosilicates, aluminosilicates, lead silicates, glass ceramic materials, or high strain-point glass-ceramic materials.

10. A glass article comprising a copper alumino-silicate glass solder with a coefficient of thermal expansion within the range of $20\text{--}82 \times 10^{-7}/^{\circ}\text{C}$.
5
11. A sealed glass article that contains temperature sensitive electrical components, where said glass article comprises a copper alumino-silicate glass solder having a coefficient of thermal expansion in the range of $20\text{--}82 \times 10^{-7}/^{\circ}\text{C}$ over the temperature range of 25-500°C, and a softening point in the range of 660-1000°C.
10
12. The sealed glass article of Claim 11, wherein said article is selected from the group consisting of: lighting devices, optical components, telecommunication devices, flat panel displays, or liquid crystal display devices.
15
13. A sealed device comprising a seal of copper alumino-silicate glass having a coefficient of thermal expansion in the range of $20\text{--}82 \times 10^{-7}/^{\circ}\text{C}$ over the temperature range of 25-500°C, and a softening point in the range of 660-1000°C.
20
14. The sealed device of Claim 13, wherein said device is selected from the group consisting of: lighting devices, optical components, telecommunication devices, flat panel displays, or liquid crystal display devices.
25
15. A lighting device envelope comprising a copper alumino-silicate glass solder having a coefficient of thermal expansion in the range of $20\text{--}82 \times 10^{-7}/^{\circ}\text{C}$ over the temperature range of 25-500°C, and a softening point in the range of 660-1000°C.
30

16. An optical component glass comprising a copper alumino-silicate glass solder having a coefficient of thermal expansion in the range of 20-82 x $10^{-7}/^{\circ}\text{C}$ over the temperature range of 25-500°C, and a softening point in the range of 660-1000°C.
- 5
17. A method of sealing glass articles comprising:
- a) providing a sealing glass with a coefficient of thermal expansion in the range of 25 – 82 x $10^{-7}/^{\circ}\text{C}$, wherein said sealing glass has a form, wherein the form is one of the following: a frit, paste, bulk glass, disk, washer, cane, tube, ribbon, or fiber;
- 10 b) providing an article having at least one joint and heat sensitive component, said article having a low-medium to high coefficient of thermal expansion;
- c) placing said sealing glass into said joint that needs to be soldered in said article;
- 15 d) exposing said sealing glass to infrared irradiation or any other source that emits long wavelength energy of 1 micron or longer, thereby heating said sealing glass to the point of melting; and
- e) melting said sealing glass without decomposition or degradation of said heat-sensitive component situated in or surrounded by said article.
- 20

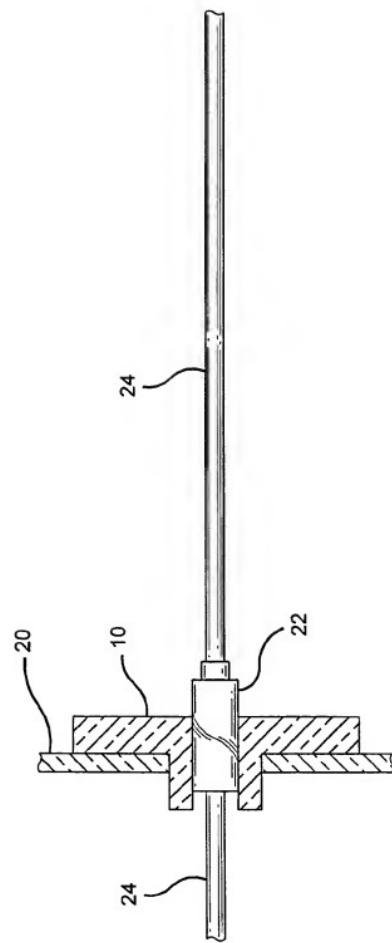


FIG. 1

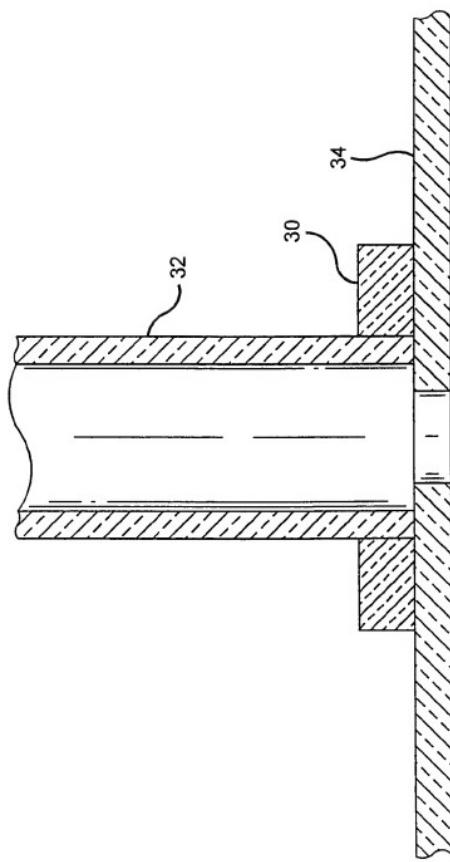


FIG. 2

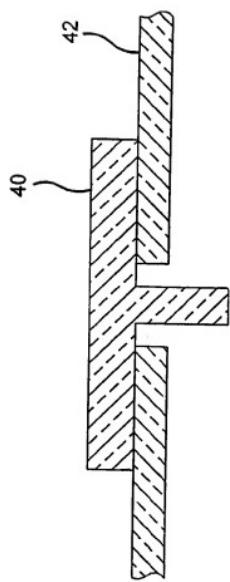


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/30225

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C03C 3/064, 3/066, 3/085, 3/091, 3/093, 8/02, 8/04, 8/06, H01J 17/18
 US CL : 501/21, 25, 26, 59, 66, 67, 69, 70, 71, 77, 79, 313/623

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 501/21, 25, 26, 59, 66, 67, 69, 70, 71, 77, 79, 313/623

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,788,165 A (FONG et al.) 29 November 1988 (29.11.1988), Abstract, col. 4, Example 9.	1-7 and 10
X	US 3,902,881 A (PIROOZ) 02 September 1975 (02.09.1975), col. 6, Example 1, col. 8, lines 62-67.	1-7 and 10
X	US 3,639,113 A (ASLANOVA et al.) 01 February 1972 (01.02.1972), Abstract, col's 3-4, table.	1-7 and 10
X	US 2,849,338 A (WHITEHURST et al.) 26 August 1958 (26.08.1958), col. 3, lines 57-64.	1-7 and 10
X	US 2,733,158 A (TEIDE) 31 January 1956 (31.01.1956), col. 1, lines 65-70.	1-7 and 10

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent published on or after the international filing date	"Y"	document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A"	document member of the same parent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

05 March 2001 (05.03.2001)

Date of mailing of the international search report

09 APR 2001

Name and mailing address of the ISA/US

 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

David Sample

Telephone No. (703)308-0661

 DEBORAH THOMAS,
Notary Public
 PARALEGAL SPECIALIST